Influence of carbon source decomposition process to CNT growth from carbon solid seeds at high temperature

阪大院工[1], 日本化薬(株)[2] °王 梦玥[1],有福 達治[2], 清柳 典子[2], 佐竹 正充[2], 井ノ上 泰輝[1],小林 慶裕[1]
Osaka Univ. [1], Nippon Kayaku [2], °M. Wang[1], M. Arifuku[2],
N. Kiyoyanagi[2], M. Satake[2], T. Inoue[1], Y. Kobayashi[1]
E-mail: wang.my@ap.eng.osaka-u.ac.jp

[Introduction] As one of factors proved to influence the formation of carbon nanotube (CNT) structure in chemical vapor deposition (CVD) system, the carbon source decomposition reactions happened in gas-phase has gained more attention recently. Among various intermediates generated from carbon source pyrolysis process, C_2 and C_4 species have been recognized as key products to enhance CNT growth efficiency [1,2]. In our previous work [3], through the usage of two-stage growth method with the injection of etchants (water vapor or carbon dioxide), the yield of high-quality CNT has been improved by the further comprehension of growth driving force and the etching effects of growth enhancer. Nevertheless, thinking about the significant influence of carbon feedstock constituent, as the first part of CVD progress, the pyrolysis process still needs efforts to illustrate and find out the crucial intermediates for promoting CNT growth. In this work, we focused on analyzing the difference of CNT growth results caused by using different carbon feedstock, C_2H_2 and C_2H_4. Based on this, the influence of gas-phase pyrolysis behavior to CNT growth at high temperature will be studied.

[Experiment] Carbon nano-onion (CNO) was formed by heating nanodiamond at 1000°C in Ar for 1 hour and works as the growth seed in CNT synthesis. To compare the growth behavior, C_2H_2 and C_2H_4 were used as the carbon feedstock independently in the two-stage growth method. In the first stage for cap formation, the partial pressure of the growth gas (C_2H_2/Ar or C_2H_4/Ar) has been adjusted through mass flow controller at 850-900ºC to balance the influence by temperature and partial pressure. Then, for the second growth stage, the temperature was increased to 1000ºC to continue growing the tube part (30 min). The partial pressure of the carbon source gas was kept as low as 0.5 Pa for C_2H_2 and 5 Pa for C_2H_4. The quality (G and D bands) and yield (G band observation frequency) of the grown CNT were characterized by Raman spectra using 633 nm excitation.

[Result and discussion] Raman spectra in Fig. 1 compare the growth behavior with different carbon feedstock utilized in two-stage growth and with/without water vapor injection. The growth condition for these samples were optimized for high quality CNT growth. Using C_2H_4 as the carbon feedstock (Fig. 1(b)), the intensity of D band, which represents the deposition of amorphous carbon (a-C) in this case, did not show any distinct decrease even after the injection of water vapor, in contrast to the case of C_2H_2 in Fig. 1(a). Such out of controlling of the a-C deposition should indicate overloading of pyrolysis intermediate species adsorbed on the growth seeds surface which is excessive to mild injection of water vapor. Figure 2 shows growth yield evaluated by G band observation frequency in each step of the growth process, namely initial growth, temperature rising, and stationary growth of CNT. In the case of C_2H_2 (Fig. 2(a)), the CNT growth has been accelerated significantly while the growth step enters into the stationary growth (1000ºC, 30min). Different behavior was observed for C_2H_4 case as shown in Fig. 2(b). Higher growth rate tends to appear at lower temperature before the stationary growth step with or without the water vapor injection. Related to the growth stage, it also could be found that the pyrolysis products of C_2H_2 prefer to enhance CNT tube formation in the stationary growth stage. As for the C_2H_4 case, such products prefer to enhance CNT cap formation in the initial growth stage, while the overloading of intermediates prevented the further tube growth process at the stationary growth step. These results indicate that the intermediates produced from gas-phase reaction will influence the CNT growth efficiency with playing roles in different growth stages.

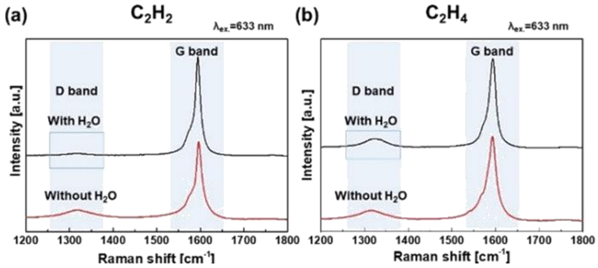

Fig. 1 CNT growth result comparison about C_2H_2 (a) and C_2H_4 (b) with or without the injection of water vapor in two-stage growth system

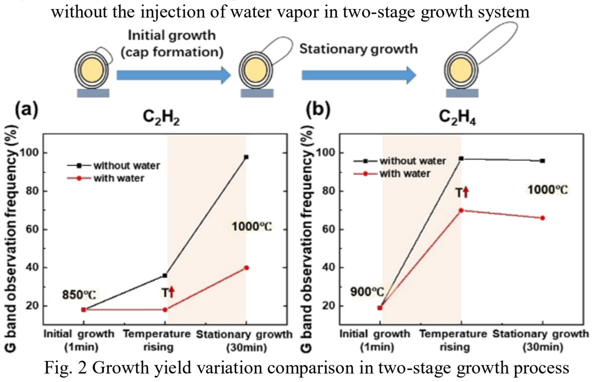

Fig. 2 Growth yield variation comparison in two-stage growth process with using C_2H_2 (a) and C_2H_4 (b) as the feedstock

[1] N. Yang et al., Carbon, 130 (2018), 607–613.
[2] D. L. Plata et al., ACS Nano, 4(2010), 7185–7192.
[3] 王梦玥他、2019 年秋期応物講演会 21a-PB1-1、王梦玥他、2020 年春期応物講演会 8p-z29-1.